ALS

Current status of resonant inelastic X-ray scattering spectroscopy (RIXS) and the need for nano-RIXS

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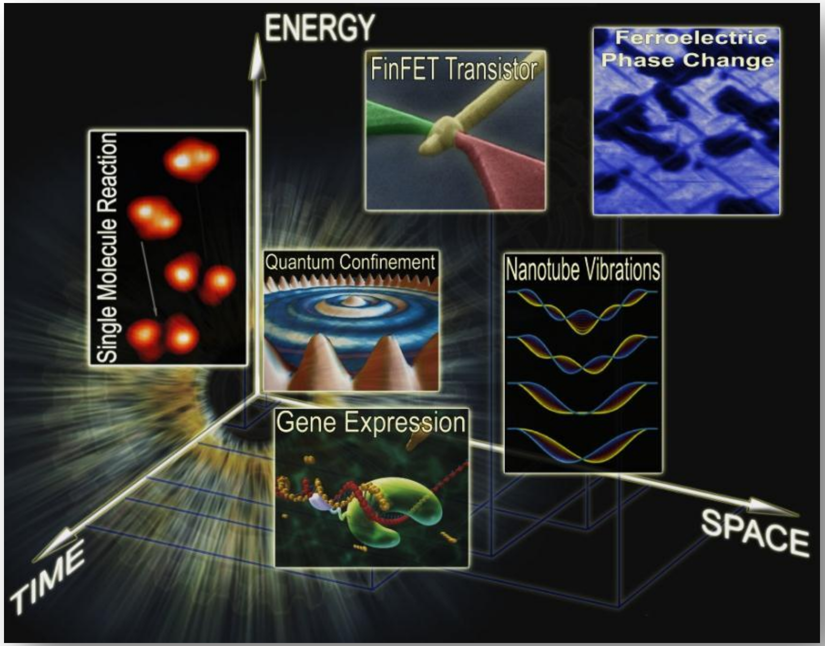
Outline

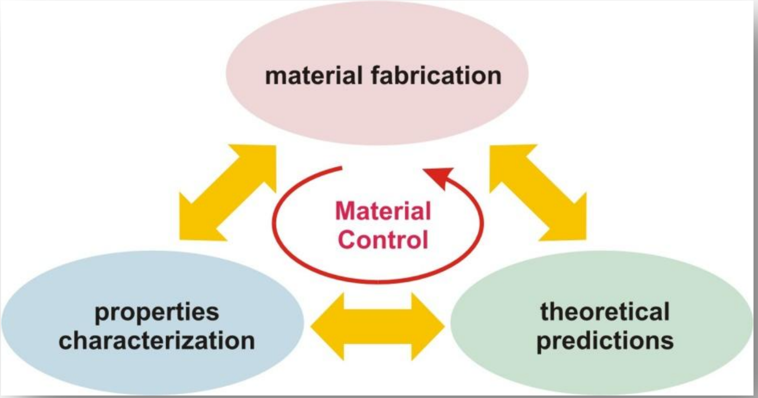
- Introduction.
- Compare different spectroscopic probes.
- Advantages and limitation of RIXS.
- Which edge to choose? TM L or M edges?
- Few examples to argue the need of nano-RIXS.
- Conclusions.

Grand challenges

DOE BES five grand challenges –

- Control materials and processes at the level of electrons.
- Synthesize materials with tailored properties.
- Exploring emergent phenomena from complex correlations.
- Master energy/information flow at nanoscale with capability rivaling living things.
- Understand materials far from equilibrium states.

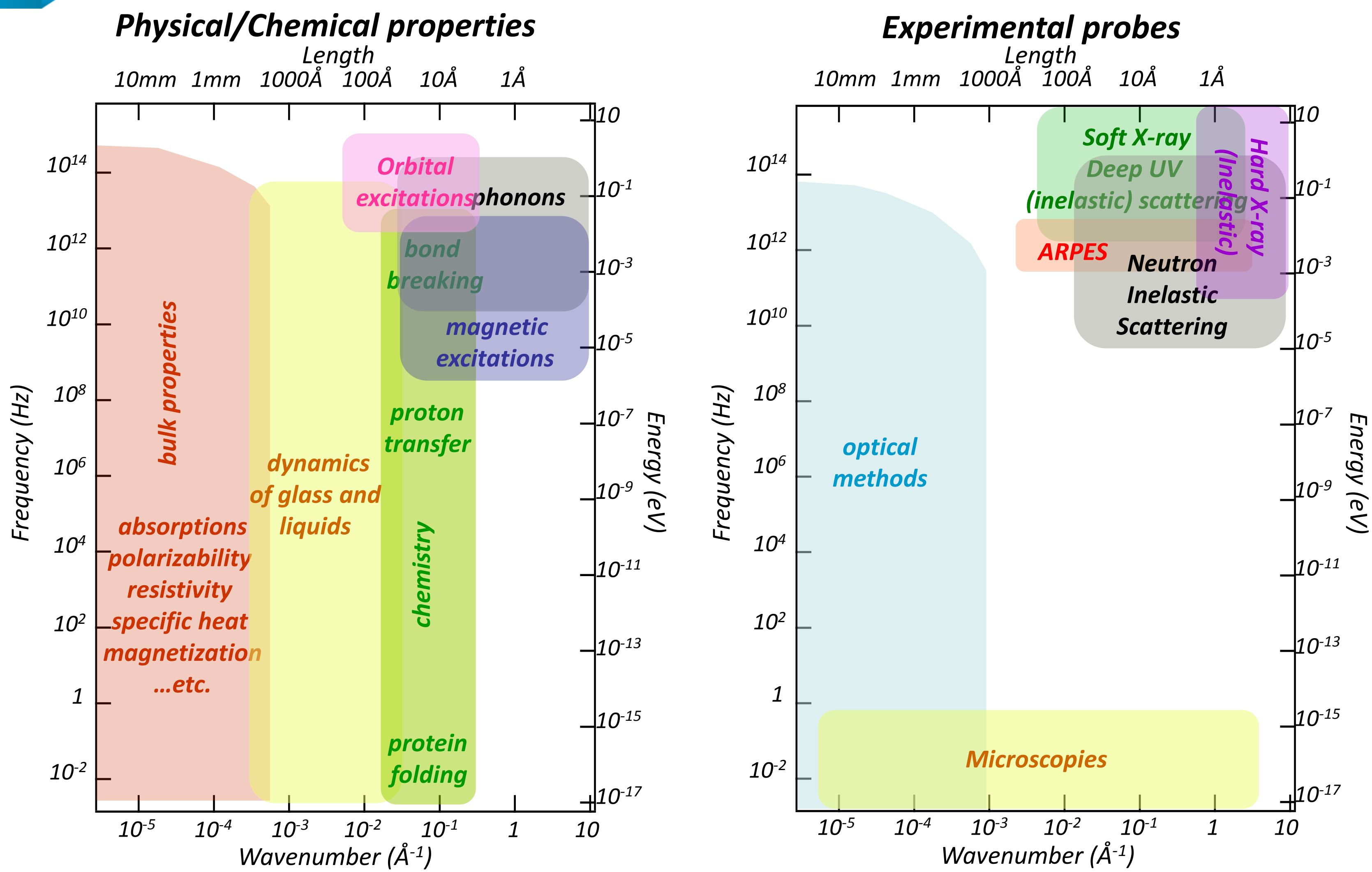




The goal is achieve the material control

Understanding complex phenomena requires sharper and sharper **tools**

Selection of experimental tools



IXS, APRES and Neutrons are the ideal tools

Comparison between different probes

Spectral Function

Single particle -

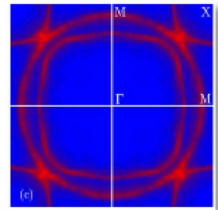
Charge: Angle-Resolved Photoemission Spectroscopy (ARPES): $I(\boldsymbol{k},\omega) \sim A(\boldsymbol{k},\omega)$

Two particles -

Spin: Inelastic Neutron Scattering (INS): spin-spin correlation $S(\boldsymbol{q},\omega)$

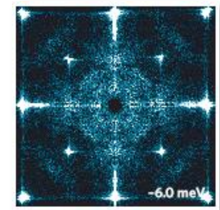
Charge: Inelastic X-ray Scattering (IXS): charge-charge correlation $S(\boldsymbol{q},\omega)$

k or q space

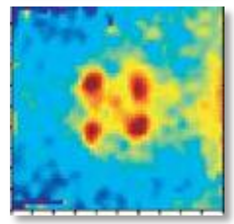


FT-STS

r-space



$Sr_3Ru_2O_7$



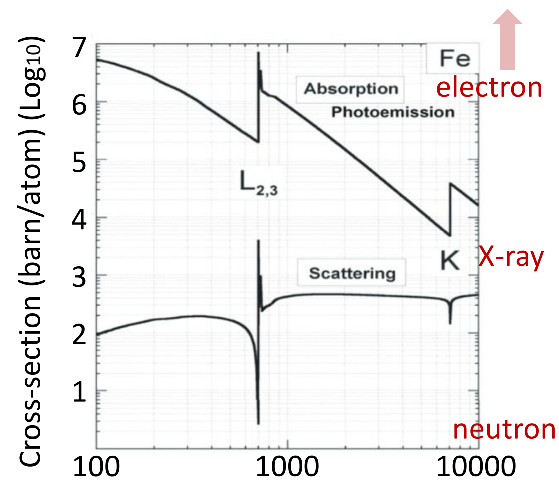
$YBa_2Cu_3O_{7-x}$

???

RIXS is a powerful probe, but needs improvements -

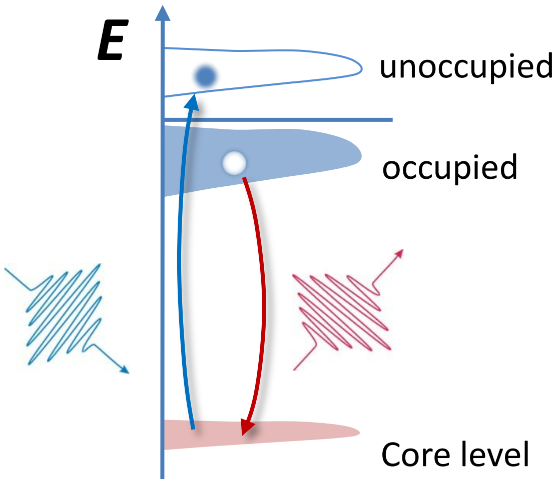
- Higher throughput
- Better resolution
- More capabilities

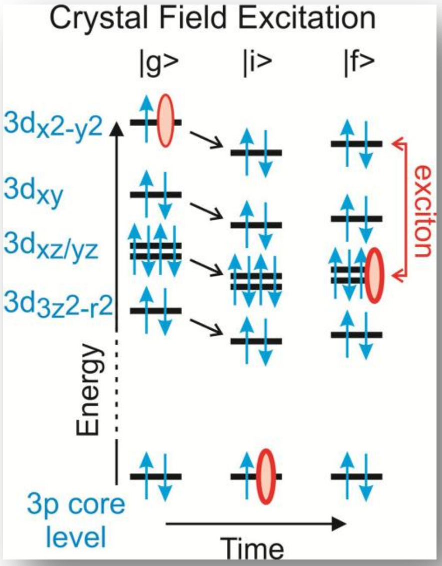
	Relative cross-section	Resolving power (E/ΔE)	Energy resolution (ΔE)	Energy range (eV)
ARPES (electron)	>10^4	10eV/1meV ~ 10^5	1meV	~ hν (100eV)
INS (neutron)	<<1	100meV/0.1meV ~ 10^3	0.1meV	~1eV
RIXS (photon)	1	1-10keV/100meV ~ $10^{4\text{-}5}$	100meV (~**10meV**)	~hν (keV)



J. Stohr

RIXS spectroscopy





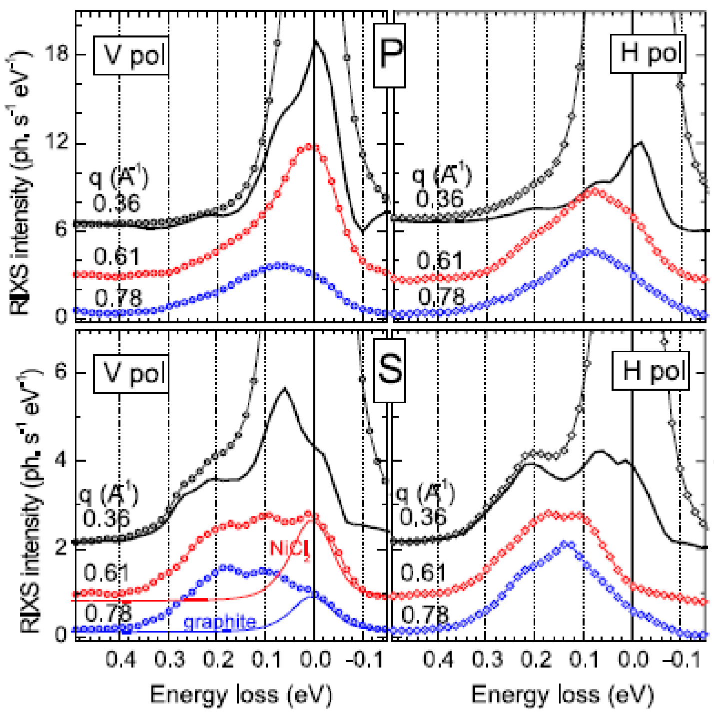
Advantages of RIXS

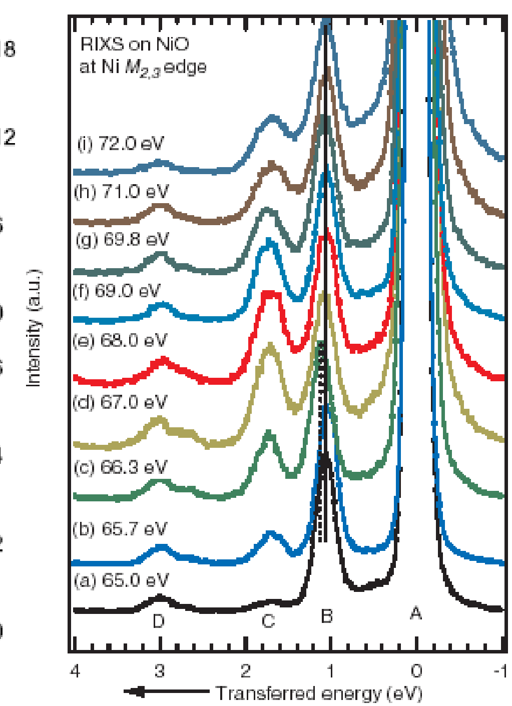
- Directly coupled to charge degree of freedom.
- Bulk sensitive – study interface properties; *in-situ* studies.
- Charge neutral process – works with presence of electric/magnetic field.
- Not limited by optical transition rule – *dd* excitations.
- Finite momentum-transfer – study indirect bandgap and exciton dispersions.
- Resonance effect - resonance enhancement of the electronic contribution and elemental selectivity.
- Symmetry selective – polarization dependence.
- Not limited by core-hole lifetime – ΔE can be greatly improved.
- Fast dynamics – internal clock set by the core-hole when incident energy is detuned away from elemental edges.

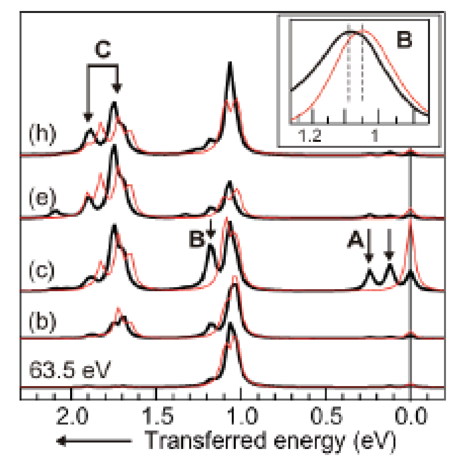
… but RIXS has certain limitations (resolution and throughput)

RIXS at different edges

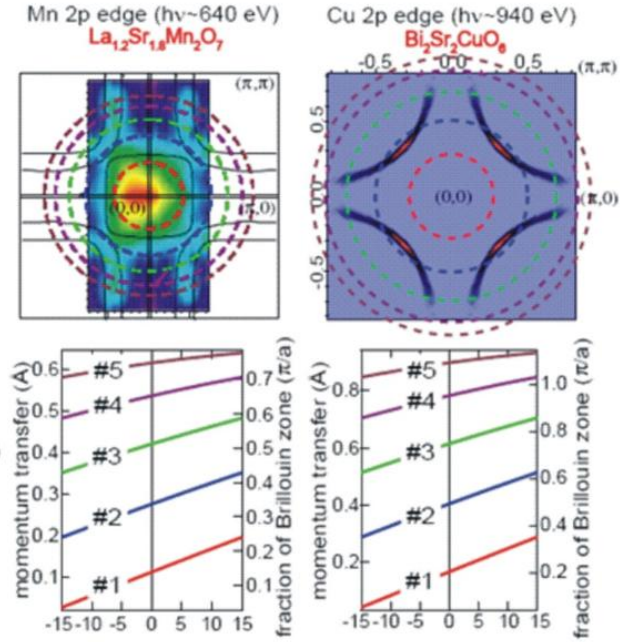
Edge	Energy range	Resolving power for 10meV	pros	cons
L	500eV ~ 1keV	1keV/10meV = 10^5	large Δq small elastic peak on resonance fewer branching…	large machine lower throughput (with reasonable OE)
M	50~100eV	100eV/10meV = 10^4	small Δq smaller machine larger throughput	strong elastic peak more branching



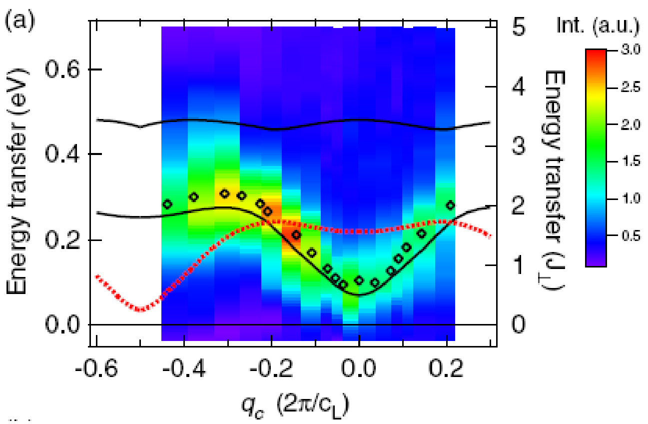




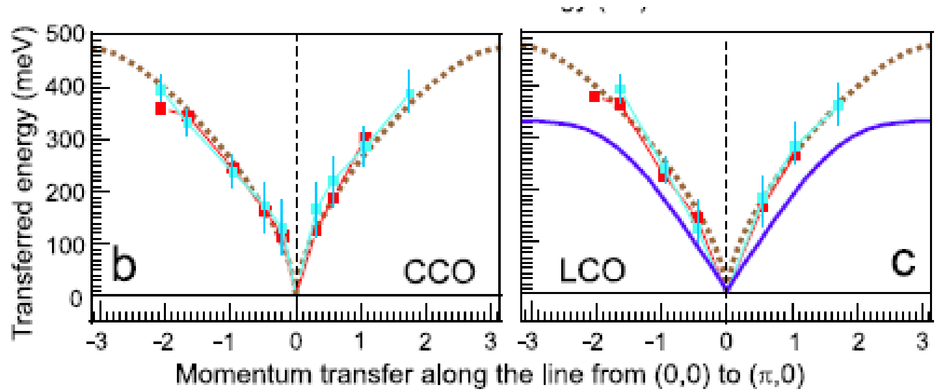
*S.G. Chiuzbaian et al. PRL **95**, 197402 (2005)*
*L. Duda et al, PRL **96**, 067402 (2006)*
*L. Braicovich et al, PRL **102**, 167401 (2009)*
*J. Schlappa et al., PRL **103**, 047401 (2009)*
G. Ghiringhelli et al. PRL 102, 027401 (2009)



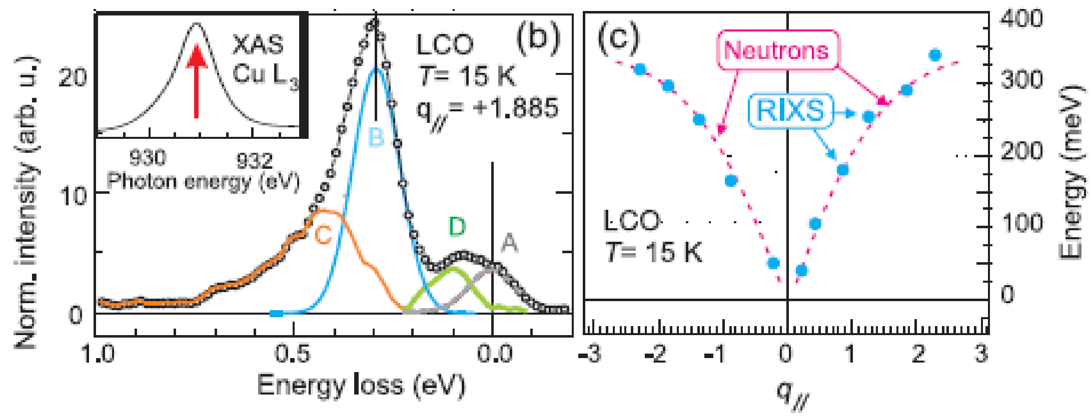
magnetic excitation (double-triplon) in $Sr_{14}Cu_{24}O_{41}$



Bi-magnon dispersion in layered cuprate (?)



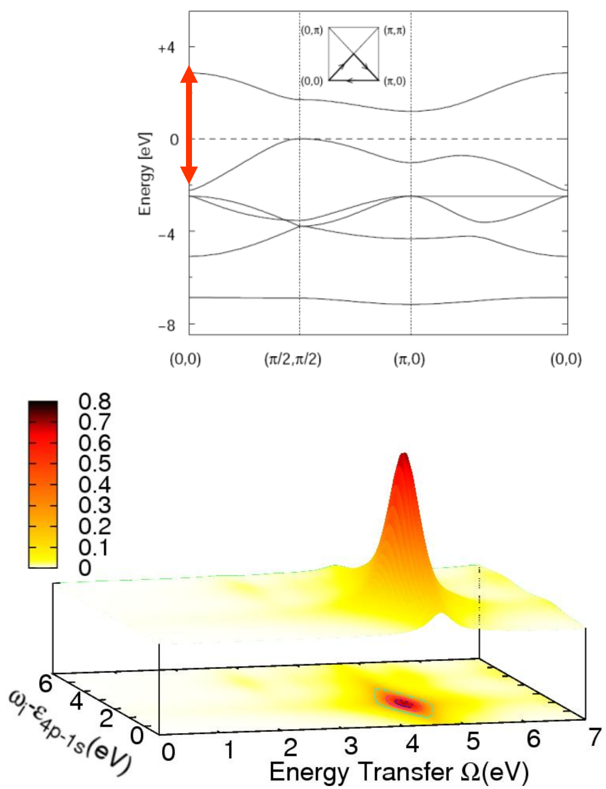
Single magnon dispersion probed by IXS and neutron



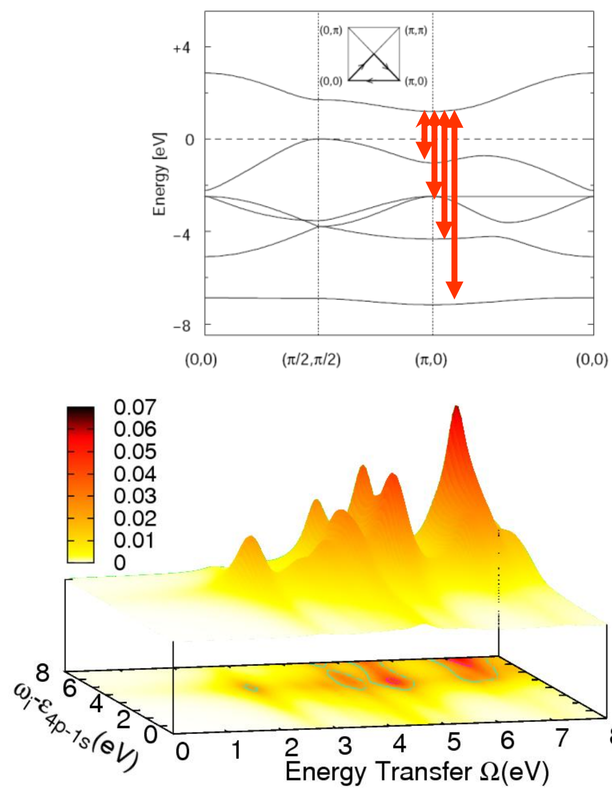
Finite momentum transfer can be helpful in exploring the dispersion of excitations; however, could be an issue as well…

Cu *K*-edge RIXS spectrum (neglecting polarization, 4p)

q_{in}=(0,0), q_{out}=(0,0), Δq =0



q_{in}=(π,0), q_{out}=(π,0), Δq=0

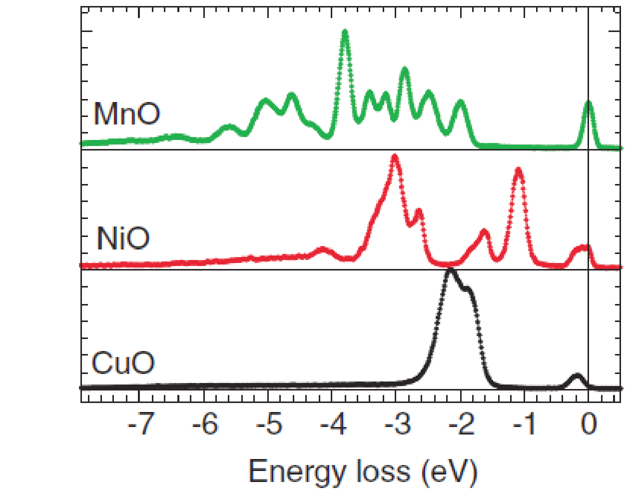


$$I(\omega_i, \Omega = \omega_i - \omega_f) \propto \sum_f \left| \sum_i \sum_{4p} \frac{\langle \psi_f | \sum_l p_{4p}^\dagger s_l \; e^{i\mathbf{q}_{\mathbf{out}}\cdot\mathbf{r}_\mathbf{l}} | \psi_{ci} \rangle \langle \psi_{ci} | \sum_j p_{4p} s_j^\dagger \; e^{i\mathbf{q}_{\mathbf{in}}\cdot\mathbf{r}_\mathbf{j}} | \psi_0 \rangle}{E_{ci} + \epsilon_{4p-1s} - E_0 - \hbar\omega_i - i\Gamma_1} \right|^2 \times \delta\left(E_f - E_i - \hbar\Omega\right)$$

RIXS is probing the wave functions of the involving states

Scientific case for nano-RIXS

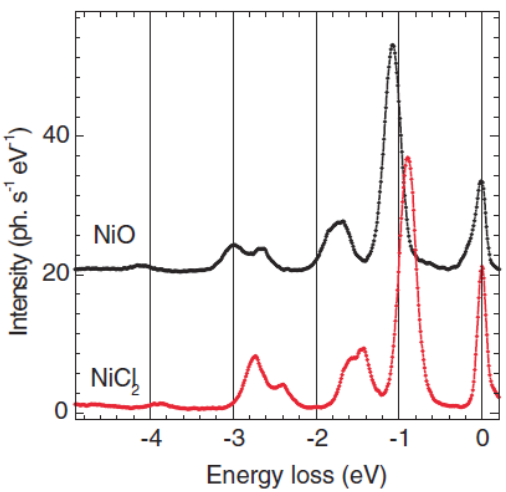
Crystal field effect



L-edge, ΔE ~100meV

- Crystal field excitation (*dd*) + Coulomb repulsion play important roles in RIXS spectra
- Sensitive to intra-atomic distance (bond length)
- Sensitive to TM valency
- Sensitive to symmetry

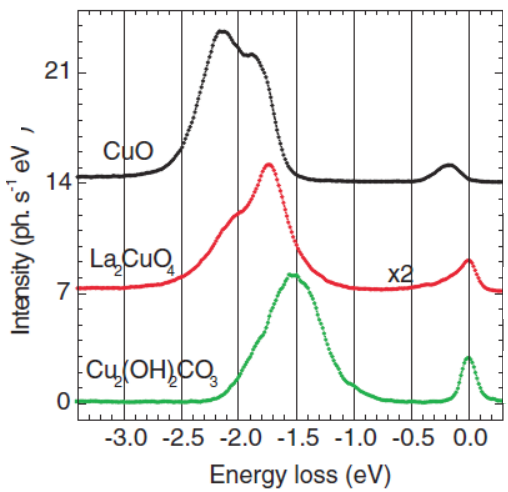
A powerful probe for local electronic environment – important for determining the electronic structures of nanoparticles



Nearly cubic symmetry Ni-O/Ni-Cl

2.08Å

2.43Å

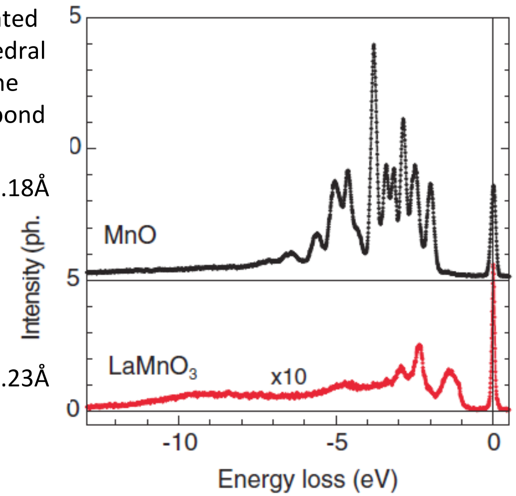


Elongated octahedral In-plane Cu-O bond length

1.68/2.18Å

1.89Å

1.92/2.23Å



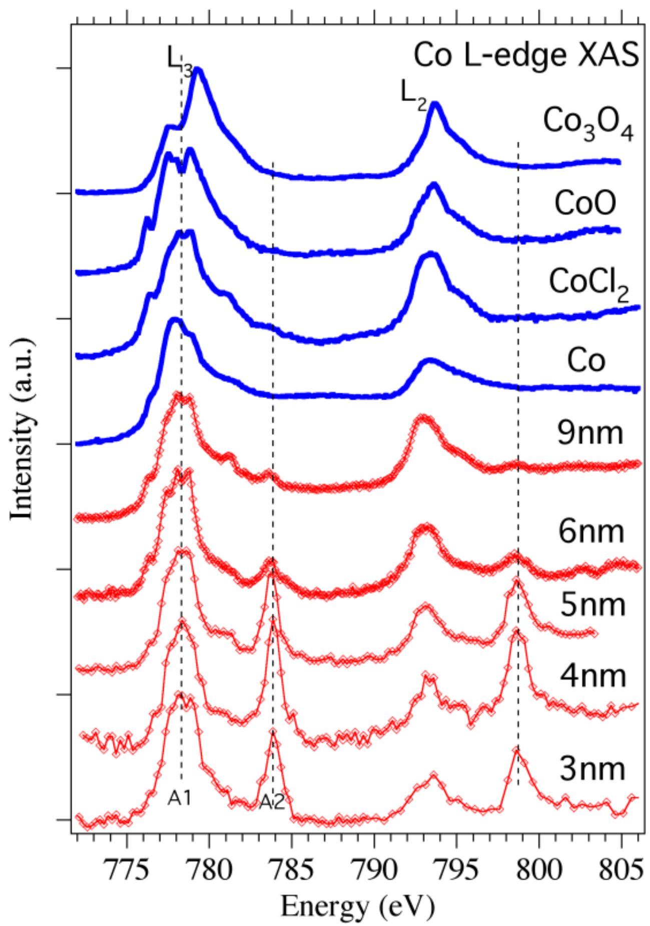
Mn2+

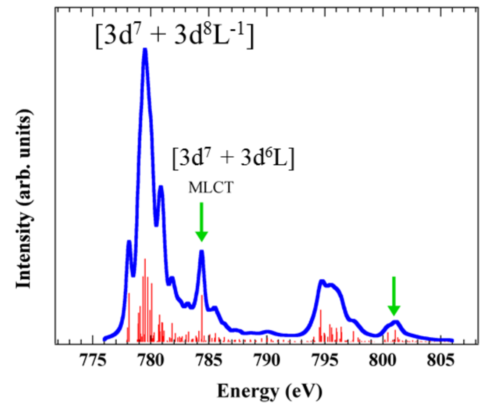
Mn3+

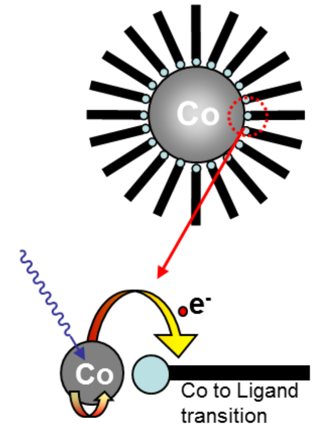
G. Ghiringhelli et al. Euro. Phys. J. ***169****, 199 (2009)*

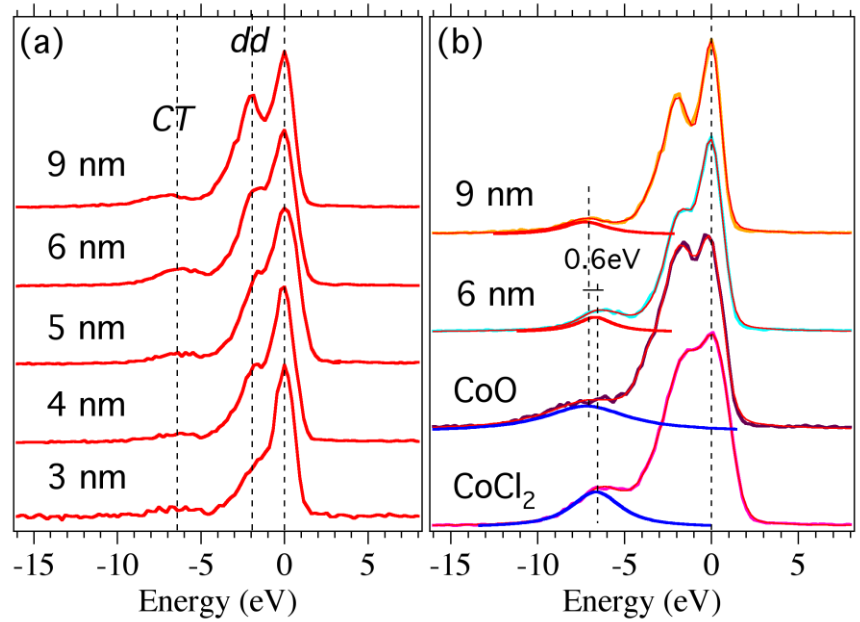
Charge transfer @ nanoscale

Co nanoparticles







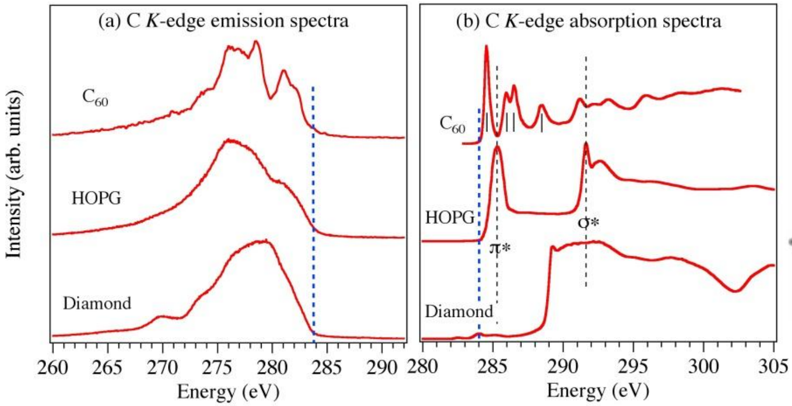


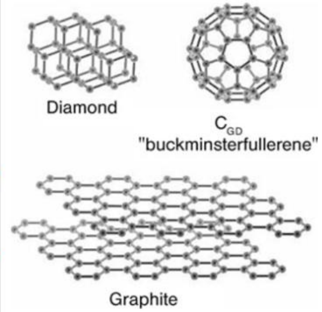
H. Liu et al. Nano Lett. ***7****, 1919 (2007)*

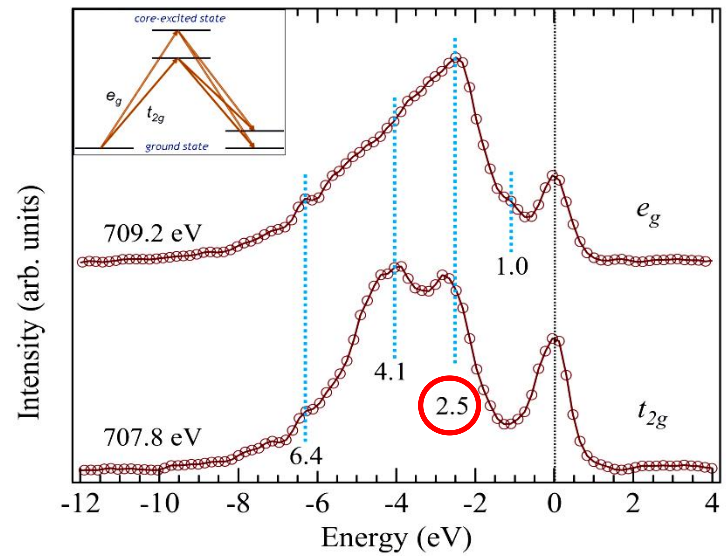
Courtesy of Jinghua Guo

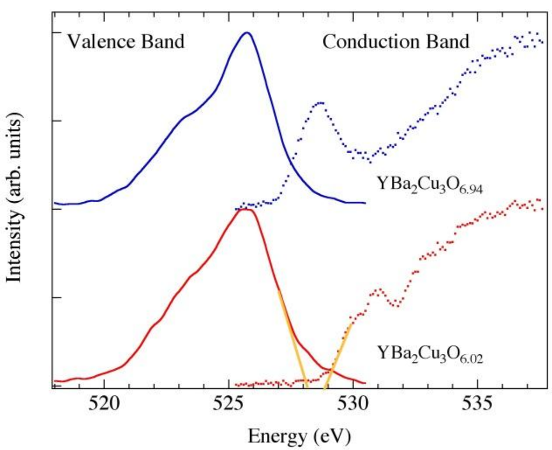
- Surfactant: *Oleic Acid, $C_{18}H_{34}O_2$ [$CH_3(CH_2)_7CH{:}CH(CH_2)_7CO_2H$]*
- Solvent: *Dichlorobenzene, $C_6H_4Cl_2$*

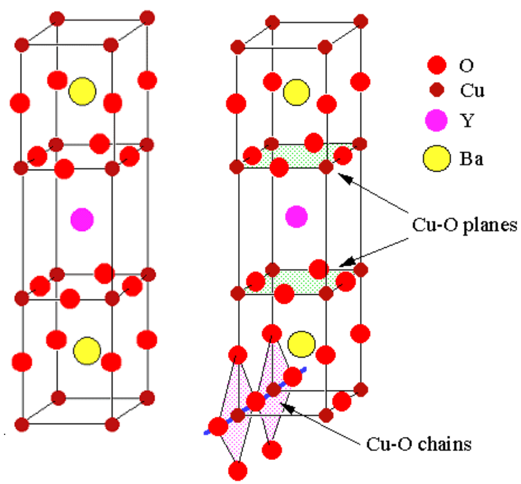
Bandgap engineering



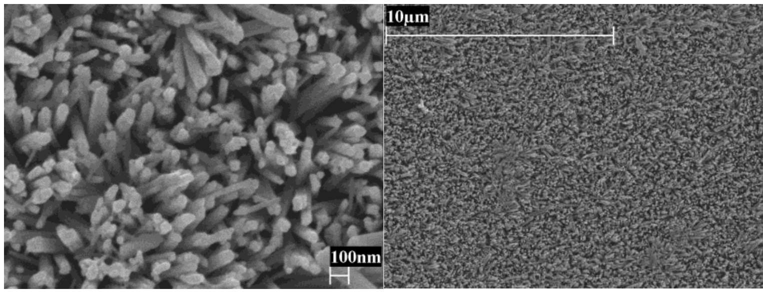


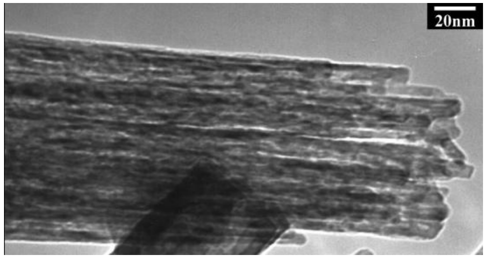






$YBa_2Cu_3O_6$ $YBa_2Cu_3O_7$

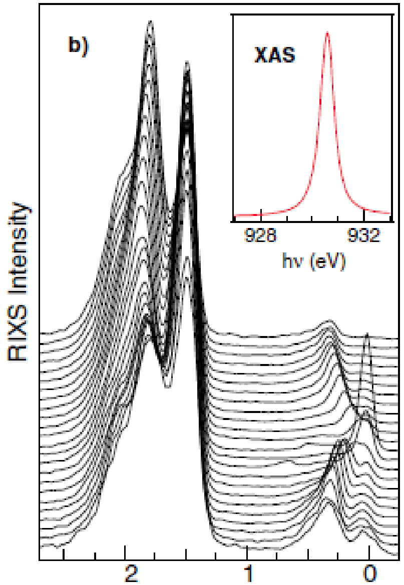




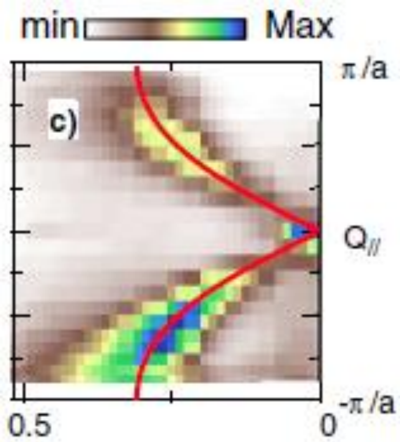
*J. Guo et al. PRB **61**, 9140 (2000)*
*J. Guo et al. Int. J. Nanotech **1**, 193 (2004)*
*L. Vayssieres et al. Adv. Mat. **17**, 2320 (2005)*
Courtesy of Jinghua Guo

Elementary excitations in correlated systems

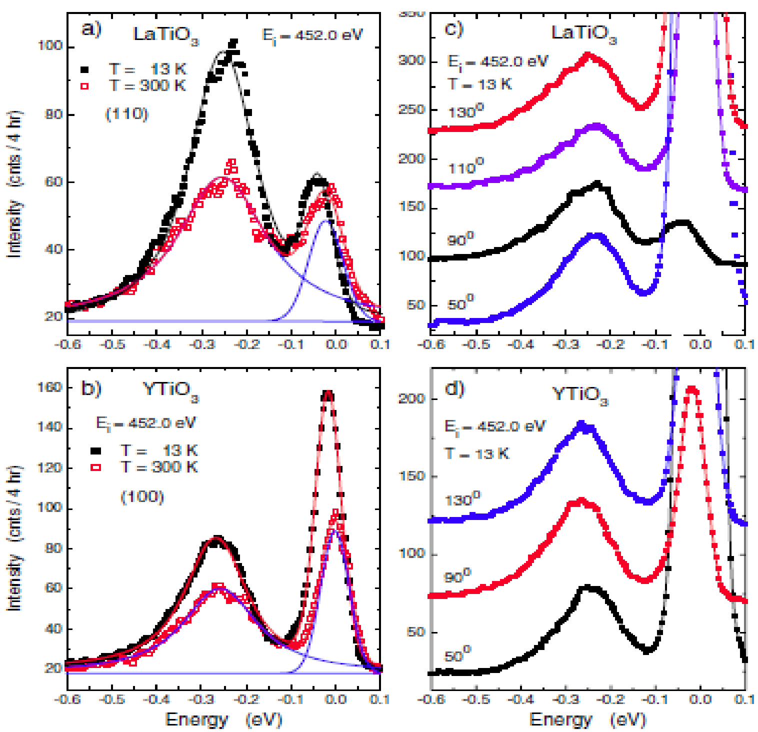
Elementary excitations

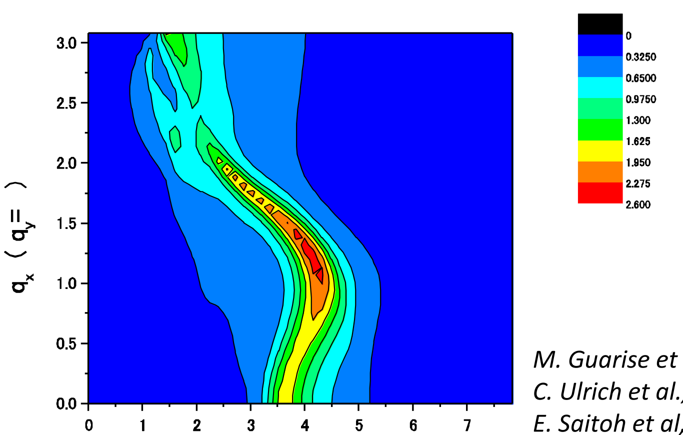


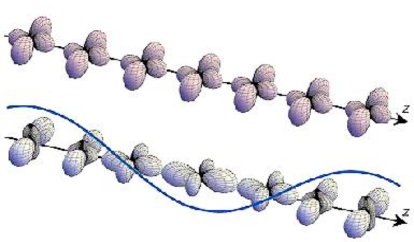
Magnon in 2D spin
1/2 $Sr_2CuO_2Cl_2$

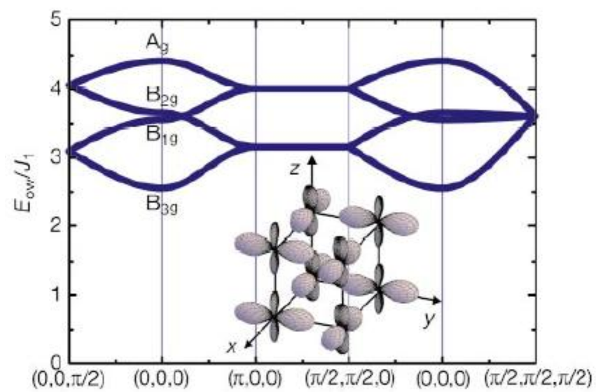


Orbital excitation - titanates





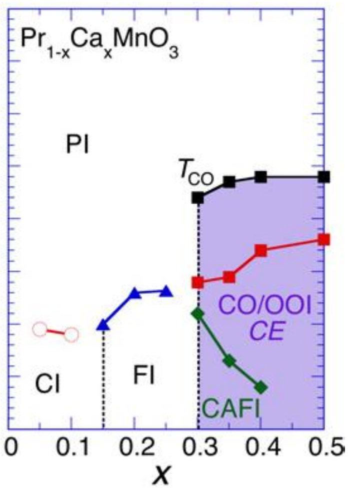


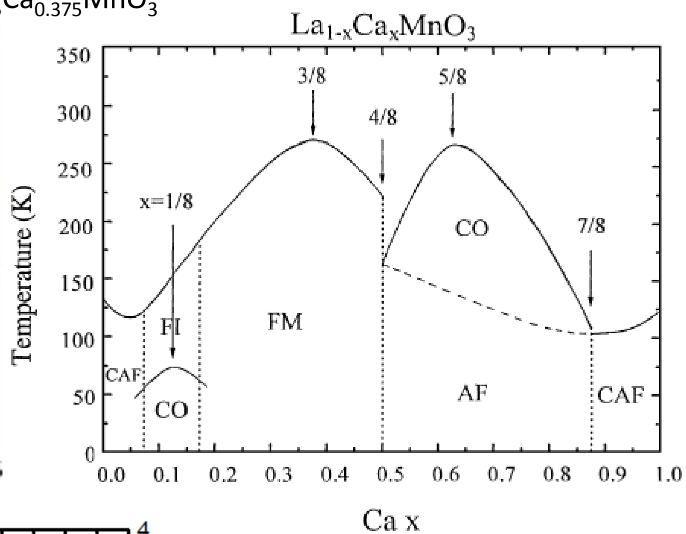


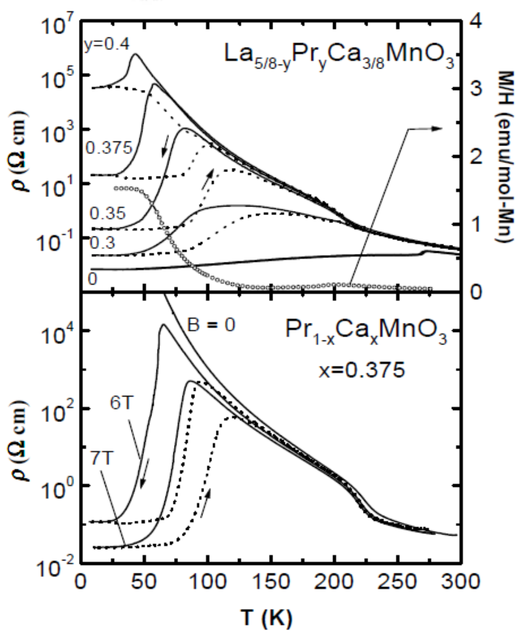
*M. Guarise et al. PRL **105**, 157006 (2010)*
*C. Ulrich et al., PRL **103**, 107205 (2009)*
*E. Saitoh et al, Nature **410**, 180 (2001)*

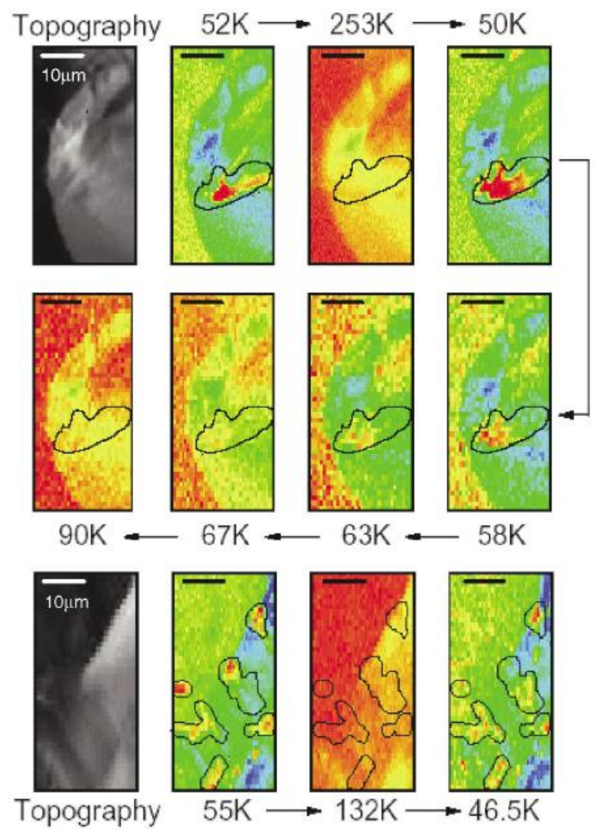
Strong phase separation

$La_{0.25}Pr_{0.375}Ca_{0.375}MnO_3$









- Strong memory effect
- Kinetic arrest due to lattice distortion

Strong phase separation in correlated systems makes the identification of the origin of excitations much harder

*D.D. Sarma et al. PRL **93**, 097202 (2004)*

Conclusion

- Nano-RIXS is a powerful probe for studying local electronic structures – if we have the energy resolution and/or flux (near elastic peak and around crystal field excitations).
- Limitation on throughput and energy resolution will determine the scientific scope.
- Potential impact to energy science – especially in the *in-situ* research.
- Important for understanding correlated electron system when electronic phase separation dominates.

Thank you